Committee of the Russian Federation
for Patents and Trademarks

DESCRIPTION OF INVENTION
for Inventor's Certificate
PATENT NO. SU 1 721 997 A1

Int. Cl.[6]:	C 03 B 37/023
Filing No.:	4808456/33
Filing Date:	April 2, 1990
Publication Date:	June 20, 1996

METHOD OF FIBERGLASS IR LIGHT PIPE PRODUCTION

Inventors: G. G. Devyatykh
M. F. Churbanov
I. V. Skripachev
G. E. Snopatin
V. P. Kolpashnikov
V. A. Shipunov

Applicant: Institut khimii vysokochistykh veshchestv AN SSSR

References: A. M. Bagrov, P. I. Baikalov et al., "Fiber light guides for the middle IR range based on As-S and As-Se with optical losses less than 1 dB/m," Kvantovaya elektronika, 1983, Vol. 10, No. 9, pp. 1906-1907

(57) Abstract:
FIELD: instrument-making industry, electronic and optical equipment. SUBSTANCE: highly purified arsenic, sulfur and selenium are melted together under temperature of 550 - 850 C in vacuumized quartz tube for 8 - 10 hours. Arsenic and sulfur are introduced in the form of monosulfide of arsenic, that is preliminary purified by vacuum distillation with specific speed of evaporation of (0.8 - 1.0)x10^{-3} g/cm^2 s. Light pipe is drawn from molten bath of produced chalcogenide glass. EFFECT: decreased optical losses in light pipe. 1 tbl

The invention relates to optical technology, specifically to methods of manufacturing fiber IR light guides that are promising for the transmission of the radiation energy of lasers, for example in laser surgery, in instruments for industrial diagnosis of electronic devices and energy units of transport means.

Closest in technical essence and achieved effect is a method of manufacturing a fiber IR light guide by melting glasses of highly pure sulfur, selenium and arsenic in an evacuated quartz ampule at 750-800°C for 8-10 h followed by slow drawing of the light guide from the melt of the resulting chalcogenide glass.

Optical losses in the light guide in the 2-8 μm range of the spectrum are 400-1000 dB/km.

A shortcoming of the method consists of the relatively high optical losses.

The goal of the invention is a reduction of optical losses in the light guide.

This goal is achieved by the fact that in the known method of manufacturing a fiber IR light guide by melting highly pure arsenic, sulfur and selenium in an evacuated quartz ampule for 8-10 h followed by drawing a light guide from the melt of chalcogenide glass that is produced, arsenic and sulfur are added to [sic; as] arsenic monosulfides purified beforehand by vacuum distillation at a specific evaporation rate of (0.8-1.0) x 10^{-3} g/cm^2·sec, and the melting is carried out at 550-650°C.

The minimum optical losses in the light guide produced by the proposed method are 40-100 dB/km in the 2-8 μm wavelength range.

Purification by vacuum distillation at a specific evaporation rate of (0.8-1.0) x 10^{-3} g/cm^2·sec makes possible efficient purification of the arsenic monosulfide to remove heterophase microinclusions, hydrogen- and oxygen-containing impurities (H_2S, H_2O, As_2O_3, CO_2, etc.). The specific evaporation rate of (0.8-1.0) x 10^{-2} [sic] g/cm^2·sec and the temperature of 550-650°C at which melting is carried out were experimentally similar [sic; determined] and, as was shown by experiment, are the most optimal for achieving the goal of the invention.

At an evaporation rate of less than 0.8 x 10^{-3} g/cm^2·sec the arsenic monosulfide converts to a solid, which in this case distills in a sublimation mode. Purification of arsenic monosulfide by sublimation is inefficient. The minimum optical losses in a light guide made using arsenic monosulfide purified by vacuum distillation at a specific evaporation rate less than 0.9 x 10^{-3} g/cm^2·sec are 400-500 dB/km at wavelengths of 2-8 μm. Distilling arsenic monosulfide at an evaporation rate greater than 1.0 x 10^{-3} g/cm^2·sec is also inefficient because of the increase of splash entrainment during distillation. Optical losses in a light guide made using arsenic monosulfide purified by distillation at an evaporation rate greater than 1.0 x 10^{-3} g/cm^2·sec are 400 dB/km in the 2-8 μm wavelength range.

At a glass melting temperature less than 550°C, homogenization of the melt becomes difficult, and because of its high viscosity the glass turns out to be nonuniform in composition, which leads to an increase of nonselective absorption due to scattering of radiation over the entire spectral transmission range. In turn this leads to an increase of optical losses to 3000-5000 dB/km at wavelengths 2-8 μm. At a melting temperature greater than 650°C there is a noticeable increase of the intensity of impurity absorption of hydrogen-containing impurities (OH and SH groups) at wavelengths 2.7, 4.02 and 6.3 μm (optical losses in the light guide at these wavelengths are more than 3000 dB/km in this case), which limits the range of use of such light guides, for example for transmission of the energy of YAG:Er^{3+} (λ = 2.94 μm), HF, DF and CO lasers.

Example 1. 600 g arsenic monosulfide are put into an ampule of highly pure quartz glass and purified by vacuum distillation at an evaporation rate of 0.9 x 10^{-3} g/cm^2·sec and 540 g distillate are obtained. 81 g sulfur are added to the purified monosulfide, i.e., the amount needed to obtain a glass making composition As_2S_3. This mixture is melted at 550°C for 10 h in an evacuated sealed ampule of highly pure quartz glass for 8 h [sic]. A fiber light guide is drawn from the resulting melt. The optical properties in the light guide are determined by IR spectroscopy by the fracture method [unconfirmed translation]. Minimum optical losses in the light guide are 44 dB/km in the 2-8 μm range.

Example 2. Experiment conditions as in Example 1, only the As_4S_4 is purified by vacuum distillation at an evaporation rate of 1.0 x 10^{-3} g/cm^2·sec. Minimum optical losses in the light guide are 100 dB/km in the 2-8 μm range.

Example 3. Experiment conditions as in Example 1, only As_4S_4 is purified by vacuum distillation at an evaporation rate of 0.8 x 10^{-3} g/cm^2·sec. Minimum optical losses in the light guide are 270 dB/km in the 2-8 μm range.

Example 4. Experiment conditions as in Example 1, only the As_4S_4 is purified by vacuum distillation at an evaporation rate of 0.7 x 10^{-3} g/cm^2·sec. Distillation is carried out in a sublimation regime. Minimum optical losses in the light guide are 500 dB/km in the 2-8 μm range.

Example 5. Experiment conditions as in Example 1, only the As_4S_4 is purified by vacuum distillation at an evaporation rate of 1.1 x 10^{-3} g/cm^2·sec. Minimum optical losses in the light guide are 400 dB/km in the 2-8 μm range.

Example 6. Experiment conditions as in Example 1, only the mixture of As_4S_4 + S is heated to 650°C. The minimum optical losses in the light guide are 88 dB/km in the 2-8 μm range.

Example 7. Experiment conditions as in Example 1, only the As_4S_4 + S mixture is heated to 540°C. Glass that is not uniform in composition is obtained. The minimum optical losses in the light guide are 3000 dB/km in the 2-8 μm wavelength range.

Example 8. Experiment conditions as in Example 1, only the As_4S_4 + S mixture is heated to 660°C. Optical losses rise to 3000 dB/km at wavelengths 2.7, 4.05 and 6.3 μm. Minimum optical losses are 200 dB/km in the 2-8 μm range.

Example 9. 600 g As_4S_4 are put into an ampule of highly pure quartz glass and purified by vacuum distillation at an evaporation rate of 0.9 x 10^{-3} g/cm^2·sec, and 540 g distillate As_4S_4 are taken as purified product. 299 g selenium is added to the purified product, i.e., the amount needed to produce a glass-making composition $As_4S_4Se_3$. This mixture is melted at 550°C in an evacuated sealed ampule of highly pure quartz glass. A fiber light guide is drawn from the resulting melt. The minimum optical losses in the light guide were determined by IR spectroscopy by the fracture method. The minimum optical losses in the light guide are 76 dB/km in the 2-8 μm range.

Example 10. Experiment conditions as in Example 9, only the As_4S_4 is purified by vacuum distillation at an evaporation rate of 1.0 x 10^{-3} g/cm^2·sec. The minimum optical losses are 93 dB/km in the 2-8 μm range.

Example 11. Experiment conditions as in Example 9, only the As_4S_4 is purified by vacuum distillation at an evaporation rate of 0.8 x 10^{-3} g/cm^2·sec. The minimum optical losses are 320 dB/km in the 2-8 μm range.

Example 12. Experiment conditions as in Example 9, only the As_4S_4 is purified by vacuum distillation at an evaporation rate of 1.1 x 10^{-3} g/cm^2·sec. The minimum optical losses are 520 dB/km in the 2-8 μm range.

Example 13. Experiment conditions as in Example 9, only the As_4S_4 + S mixture is heated to 650°C. The minimum optical losses in the light guide are 84 dB/km in the 2-8 μm range.

Example 14. Experiment conditions as in Example 9, only the As_4S_4 + S mixture is heated to 540°C. A glass that is not uniform in composition is obtained. The minimum optical losses in the light guide are 7000 dB/km in the 2-8 μm range.

Example 15. Experiment conditions as in Example 9, only the As_4S_4 + S mixture is heated to 660°C. An increase of optical losses up to 4500 dB/km is observed at wavelengths 2.7, 4.05 and 6.3 μm. Minimum optical losses are 380 dB/km in the 2-8 μm range.

The data from the examples are summarized in the table.

It can be seen from the table that light guides with minimum optical losses of 40-100 dB/km in the 2-8 μm wavelength range are obtained when arsenic monosulfide is purified beforehand by vacuum distillation at an evaporation rate of (0.9-1.0) x 10^{-3} g/cm^2·sec and

melting of the glass is conducted at 550-650°C (see Examples 1, 2, 9, 10, 13). In the purification of As_4S_4 by vacuum distillation at a specific evaporation rate below 0.8×10^{-3} g/cm^2·sec or above 1.0×10^{-3} g/cm^2·sec the optical losses in the light guide increase sharply (see Examples 3, 4, 5, 11, 12). The synthesis of glass at a temperature below 550°C and above 650°C also leads to a sharp increase of optical losses (see Examples 7, 8, 14, 15).

Compared to the prototype, the proposed method makes it possible to reduce optical losses in the light guide from 400-1000 dB/km to 40-100 dB/km in the 2-8 μm region of the spectrum. TTT1 [sic]

Claim

A method of making a fiber IR light guide by melting highly pure arsenic, sulfur and selenium in an evacuated quartz ampule for 8-10 h followed by drawing of a light guide from the melt of chalcogenide glass that is obtained, which is distinguished by the fact that, with the goal of reducing the optical losses in the light guide, arsenic and sulfur are added arsenic monosulfite [sic], which has been purified beforehand by vacuum distillation at a specific evaporation rate of $(0.8\text{-}1.0) \times 10^{-3}$ g/cm^2·sec, and melting is carried out at 550-650°C.

Conditions for producing chalcogenide glasses of the As-S and As-S-Se systems and the minimum optical losses in light guides that are achieved

1 Состав стекла	2 Удельная скорость дистилляции г/см²·с	3 Температура синтеза стекла, °С	4 Минимальные оптические потери в диапазоне 2-8 мкм, дБ/км
1 As_2S_3	$0{,}9\cdot10^{-3}$	550	44
2 As_2S_3	$1{,}0\cdot10^{-3}$	550	100
3 As_2S_3	$0{,}8\cdot10^{-3}$	550	270
4 As_2S_3	$0{,}7\cdot10^{-3}$	550	500
5 As_2S_3	$1{,}1\cdot10^{-3}$	550	400
6 As_2S_3	$0{,}9\cdot10^{-3}$	650	88
7 As_2S_3	$0{,}9\cdot19^{-3}$	540	3000
8 As_2S_3	$0{,}9\cdot10^{-3}$	660	200
9 $As_4S_4Se_3$	$0{,}9\cdot10^{-3}$	550	76
10 $As_4S_4Se_3$	$1{,}0\cdot10^{-3}$	550	93
11 $As_4S_4Se_3$	$0{,}8\cdot10^{-3}$	550	320
12 $As_4S_4Se_3$	$1{,}1\cdot10^{-3}$	550	520
13 $As_4S_4Se_3$	$0{,}9\cdot10^{-3}$	650	84
14 $As_4S_4Se_3$	$0{,}9\cdot10^{-3}$	540	7000
15 $As_4S_4Se_3$	$0{,}9\cdot10^{-3}$	660	380

Key:
1. Composition of glass
2. Specific distillation rate, $g/cm^2 \cdot sec$
3. Glass synthesis temperature, °C
4. Minimum optical losses in 2-8 μm range, dB/km